

**ROOM TEMPERATURE OF LIQUIFIED PETROLEUM GAS (LPG) SENSOR
BASED ON p-La₂O₃/n-Fe₂O₃**

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I declare that this thesis entitled 'Room Temperature Liquefied Petroleum Gas Sensor Based on p-La₂O₃/n-Fe₂O₃' is the results of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted candidature of any degree.

Signature :

Name :

Date :

Special dedicated to my beloved mother and father

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ABSTRACT

Recently, owing to environment and safety aspect, interest in utilization of gas sensor is increasing. Gas sensor is used to detect hazardous gas in order to avoid it from spread to the environment. Lanthanum oxide and iron (III) oxide was chosen because of their availability and cost effective. Performance of using lanthanum oxide and iron (III) oxide as sensing element were investigated. Detection of liquefied petroleum gas in this research reported has a very long response time due to the chemical properties of lanthanum oxide. The p-La₂O₃/n-Fe₂O₃ sensor has detected the LPG 20 minutes after start flowing the gas inside the modified plastic bottle. This paper also describe the study on thermal stability of each substrate has been done using Thermogravimetric Analysis (TGA). Thermogravimetric Analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. Lanthanum oxide shows that at 800⁰C their original form will be transform into another phase of oxide such as LaO and LaO₂. Iron (III) oxide still remains their original form to the end of the sintered.

ABSTRAK

Dewasa ini, disebabkan oleh factor alam sekitar dan juga aspek keselamatan, kehendak terhadap penggunaan pengesan gas kian meningkat. Pengesan gas digunakan untuk mengesan gas-gas yang berbahaya daripada terbebas ke persekitaran. Prestasi penggunaan lanthanum oksida dan ferum (III) oksida sebagai alat pengesan dikaji. Lanthanum oksida dan ferum oksida dipilih disebabkan oleh mudah di dapati dan juga harganya yang efektif. Pengesanan liquefied petroleum gas di dalam kajian ini dilaporkan mengambil masa yang agak panjang disebabkan oleh sifat kimia lanthanum oksida. Alat pengesan p-La₂O₃/n-Fe₂O₃ telah mengesan LPG selama 20 minit selepas gas itu dialirkan ke dalam bekas plastik. Selain itu, di dalam laporan ini juga menerangkan kajian terhadap kestabilan therma setiap bahan menggunakan thermogravimetric analisis (TGA). Thermogravimetric analisis ini adalah sejenis ujian terhadap prestasi sampel untuk melihat perubahan di dalam berat disebabkan oleh perubahan suhu. Kajian ini menunjukkan ketelitian terhadap tiga parameter iaitu berat, suhu dan perubahan suhu. Lanthanum oksida menunjukkan pada suhu 8000C struktur asalnya akan berubah kepada fasa oksida yang berlainan seperti LaO atau LaO₂. Manakala ferum (III) oksida pula kekal pada fasa asalnya sehingga tamat proses pembakaran.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Nowadays the semiconductor gas sensors are broadly applied to the atmosphere monitoring system, the toxic or explosive gases detection system, the chemical processing facilities, the intelligent buildings with environmental control functions and so on. Gas-sensing materials can be classified mainly into two kinds: organic and inorganic materials. Doped or undoped SnO_2 is the most studied and used among the inorganic materials, but its operation temperature is about 150°C - 350°C . It is actually have nine types of gas sensor or in other word there are nine technologies in gas sensor which is semiconductor – resistive, semiconductor – voltage, amperometric, catalytic, infrared, photo-ionization, fluorescent, surface acoustic wave and vibrating beam and capacitive. Every technology that stated above has their advantages and disadvantages. From all this technology, semiconductor is commonly used because of their better efficiency and low cost. Gas sensor main application is to detect hazardous gases that can harm people when it is spread to atmosphere. So using gas sensor will be detected a leaking of hazardous gas to the atmosphere.

1.2 Problem statement

Commercial solid state gas sensors based on semiconducting metal oxide, use property that gas changing the surface charge carrier concentration of semiconductor to cause changes in its electrical conductivity. This mechanism of the detection will help to monitor hazardous gases and to detect the threshold level of gases present in the atmosphere. However, these sensors showed poor performance with respect to the sensitivity at low concentrations of gases, selectivity and long-term stability. Metal oxide also will only detect at temperature range 150⁰C to 350⁰C. The gas-sensing devices based on organic materials, such as polypyrrol, polyaniline, and metaphthalocyanines, have gas sensitivity at room temperature, but their long response time (min) due to the orderly structure limits their usage. Consequently, there is a need for development of cost effective sensors to monitor LPG at room temperature.

1.3 Objective

In current research, the objectives are:

1. To characterize fabricated semiconductor/metal oxide.
2. To detect LPG in a room temperature.

1.4 Scope of study

Based on literature review, the scope of study for this research are:

1. To design simple experimental sensor for detection of LPG.
2. To study the LPG sensing properties in a room temperature.
3. To study thermal stability of La_2O_3 and Fe_2O_3 using thermo gravimetric analysis.

1.5 Current Research

My research is to develop a cost effective sensors to monitor LPG at room temperature. This proposal used to describe a technique to form an $\text{n-Fe}_2\text{O}_3/\text{p-La}_2\text{O}_3$ hetero-junction. These characteristics in part are a requirement for further use of the devices in a variety of sensor applications. The $\text{n-Fe}_2\text{O}_3/\text{p-La}_2\text{O}_3$ hetero-junction in pellet form has been fabricated using hydraulic press.

This research will use semiconductor resistive method. This gas sensor will used $\text{n-Fe}_2\text{O}_3/\text{p-La}_2\text{O}_3$ junction as their sensing element. Lanthanum oxide has largest band gap of the rare earth oxides at 4.3 eV, while also having the lowest lattice energy, with very high dielectric constant, $\epsilon = 27$ pF/m. Lanthanum oxide has p-type semi-conducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is $10^3 \Omega \text{ cm}$.

CHAPTER 2

LITERATURE REVIEW

2.1 Type of Gas Sensor

Nowadays there are variety of gas sensor that been develop for many reasons. Each gas sensor has their advantages and disadvantages. So research has been made to maximize their ability and reduce their disadvantages. The existing gas sensor in market is like:

- (a) Hydrogen Gas Sensor
- (b) Carbon Dioxide Gas Sensor
- (c) Butane Gas Sensor
- (d) Propane and Butane Semiconductor Gas Sensor
- (e) Liquefied Petroleum Gas Sensor

2.1.1 Hydrogen Gas Sensor

A fuel cell with hydrogen energy is recently expected as a new energy source. However, because hydrogen concentration over 4% has the risk for an ignition, the development of sensors for quickly detecting the leakage of hydrogen has been advanced. At present, various types of sensors have been studied, such as Schottky diode type, field effect transistor (FET) type, etc. The characteristics of these sensors strongly depend on those of catalytic metals, because the principle of them is based on the work function change of catalytic metals. Therefore, it is essential to clarify the hydrogen adsorption mechanism on catalytic metals. FET type sensors using catalytic metals have been developed since 1975. These sensors have a number of advantages, which are room temperature operation, smaller size compared to the conventional sensors and low power consumption. Recently, we reported the fast response mechanism of the FET with platinum gate electrode (Pt-FET) to hydrogen in nitrogen. However, the detection of hydrogen in air is generally required for practical applications, therefore, it is necessary to investigate the hydrogen response mechanism to hydrogen in air in detail. This paper reports the effect of oxygen gas in air on the Pt-FET. (Yamaguchi T, 2006)

2.1.2 Carbon Dioxide Gas Sensor

The increasing number of vehicles using our roads annually has led to rising levels of pollution entering our atmosphere. The exhaust pollutants are a mixture of noxious gases and particulates. The gases include carbon monoxide, hydrocarbons oxides of nitrogen and oxides of sulphur. These pollutants are produced under different engine combustion conditions. CO is produced when fuel is not completely burned by an engine while NO_x emissions occur at elevated engine temperatures when trace substances in the fuel such as ammonia are oxidised. Carbon dioxide is also produced by motor vehicles. It is formed during the complete combustion of fuel. Although not strictly considered a pollutant, as it already exists as a trace gas in the atmosphere, excessive levels of CO₂ produced by road vehicles are considered a prime contributor to the climate change mechanism known as the “Greenhouse Effect”. (Clifford J, 2007)

A succession of increasingly stringent automotive emission control laws have been introduced by the European Commission in an attempt to reduce the levels of pollutants entering the atmosphere from road vehicles. Fig. 1 shows the reduction in acceptable levels of pollution since 1992 (the quantities are calculated for heavy goods vehicles (HGVs) and are given in g/kWh). (Clifford J, 2007)

The most common sensor used to detect automotive pollution is the Lambda sensor. The Lambda sensor operates by comparing the levels of oxygen in the exhaust with those in ambient air. If the level of oxygen in the exhaust is too low, high levels of CO and HC are produced, it signals to the engine to increase the fuel to air ratio. If the

level of oxygen is too high, high levels of Nox are produced, and it signals to the engine to decrease the fuel to air ratio. However, the Lambda sensor is not designed to quantify the levels of these pollutant gases (or carbon dioxide) leaving the engine as required by European emission laws. An additional difficulty with the Lambda sensor is that it degrades over time on contact with hot and corrosive elements in the exhaust. The net effect of this damage is that eventually the Lambda sensor will produce false readings causing extra fuel to be burnt which not only ruins fuel economy and damages the catalytic converter, but is also responsible for the production of increased levels of pollution. As a result of this the Lambda sensor must be replaced every 30,000–50,000 mile, which is much less than the lifetime of an average vehicle. (Clifford J, 2007)

In contrast to the Lambda sensor, an optical fibre sensor is immune to corrosion by chemicals as it is constructed from glass. Furthermore, the use of optical fibre allows the emitter and detector electronics to be located at a safe distance from the exhaust manifold and the small size and weight of optical fibre ensures that the system will not obstruct the flow of exhaust gases. As each pollutant gas has a characteristic optical absorption spectrum it is possible to determine which gas is present and in what quantity by analysing its unique optical spectrum. Clearly, a gas sensor based on absorption spectroscopy does not suffer from being cross-sensitive to other species present in the exhaust provided its spectrum can be uniquely defined and the spectral resolution of the detector is sufficient. Optical absorption lines occur throughout the electromagnetic spectrum. To date, most optical fibre based sensing has concentrated in the near-infrared due to the greater availability of components designed and optimised for use in the telecommunications industry. However, the fundamental absorption lines of most of the exhaust gases are located in the mid-infrared region with weaker overtones in the near-infrared. Certain pollutant gases such as nitric oxide and nitrogen dioxide have high absorption in the ultraviolet region, in addition to having fundamental

absorption lines in the mid-infrared and in recent years ultraviolet optical fibre gas sensors have been developed to detect these gases. However, the carbon gases, i.e. carbon monoxide and carbon dioxide only absorb radiation in the infrared region. Fig. 2 shows the infrared absorption of carbon dioxide between 0.2 and 5.2 μm . (Clifford J, 2007)

Recent improvements in components at the mid-infrared wavelength range have indicated that it is feasible to construct an optical fibre gas sensor suitable for use in a vehicle that operates in this spectral region. Previous mid-infrared optical fibre gas sensing reported in the literature has involved the use of expensive and bulky components such as Helium Neon lasers, Quantum Cascade Lasers, Fourier transfer infrared (FTIR) spectrometers, and cooled InSb detectors, which are not suitable for use in a vehicle. However, recent advances in mid-infrared components have included the improvement in output power of mid-infrared sources, the increased transmission and mechanical durability of mid-infrared fibre and the availability of mid-infrared detectors that do not require thermoelectric or nitrogen cooling have indicated that it should be possible to design an emission detection scheme based on mid-infrared components. Low cost mid-infrared sources such as filament emitters can provide adequate optical power when coupled to optical fibre. Chalcogenide optical fibres, which transmit in the 1–6 μm range, have attenuation losses, which compare quite favourably with other types of fibre available in this wavelength range such as silver halide fibre. Pyroelectric detectors, which do not require cooling, only respond to pulsed infrared signals and are therefore highly suitable for measuring pulsed infrared signals in the hot background exhaust environment. The pyroelectric detector can also be fitted with a narrow band optical filter to make it selective to the absorption line of the gas of interest. (Clifford J, 2007)

2.1.3 Butane Gas Sensor

Liquid petrol gas is widely used in industry and domestic appliances. Metal oxide semiconductor gas sensors have been used for domestic gas leaks detectors in house to produce an alarm at a given gas concentration. Conventional hydrocarbon gas sensors, normally operated above 300–400 °C , require the source of high electric power, and had poor selectivity to the ethanol vapor which is the main interfering gas in domestic ambience. In such places, workers can carry a portable sensor with a small battery for safety. Such sensors need for selective gas with respect to ethanol and operating at a low temperature for a longer battery life is obvious.

Several designs of sensors' construction, SnO₂-based, were proposed for achieving the selectivity, sensitivity and stability of combustion gas detection with respect to ethanol vapour such as directly doping of small amounts of noble metals (Pd, Pt, Rh and Ru) into SnO₂ a suitable filter containing noble metal catalysts method and a directly coating selective thin film on the surface of SnO₂ layer structure.

To develop a low temperature-operating combustion gas sensor, some problems such as reproducibility of output, low sensitivity, selectivity with respect to ethanol and effect of humidity should be solved because of low degree and slow rate of sulphur ions and surface reactions at a low temperature. Butane semiconductor gas sensor with low

operation temperature has been developed based on two-side construction which allows miniaturization of the sensor chip and most active catalyst Co_3O_4 .

In the present study we report the butane sensor based on laminating two-layer thick films (SnO_2 as the first layer and alumina-supported Pd catalyst as the second layer). The butane gas sensor based on a two-side construction (right side as sensing and back side as heating) which allows miniaturization of the sensor for operation at low temperature. The operation temperature, thickness of two-layer thick film, response and recovery time and the effect of humidity were investigated for the optimal condition chosen. The sensing characteristics of response linearity and long-term stability were further tested.

2.1.4 Propane and Butane Semiconductor Gas Sensor

Nowadays the semiconductor gas sensors are broadly applied to the atmosphere monitoring system, the toxic or explosive gases detection system, the chemical processing facilities, the intelligent buildings with environmental control functions and so on. One of the most broadly utilized semiconductor gas sensors is the tin oxide based sensor, which is commercialized as a world-famous product by Figaro, Japan. The Figaro sensor consists of the platinum coil heater placed inside the miniature ceramic tube. On the external surface of the tube, tin dioxide sensing layer is placed along with the contact pads contacting thin connection wires. (Kim J.H, 1997)

Even though this structure is very reliable and shows a good stability of the sensor properties, its disadvantage is high power consumption from 400 mW to 1 W due to heating of the massive ceramic tube. This level of power consumption has a limit for the sensors to be adopted in a battery operation portable device. (Kim J.H , 1997)

Through the cooperative research between Institute of Molecular Physics (RRC ‘Kurchatov Institute’, Russia) and Korea Institute of Energy Research (KIER, Korea), lower power consumption semiconductor gas sensors of thick film type were aimed to develop. As a target the power consumption of the sensors for propane/butane in air is as low as 100 mW. This level of power consumption seems to be good enough for the battery operation portable device which is able to run for about 10 h without recharging the battery. (Kim J.H., 1997)

As the basic technology for the fabrication of sensors the thick film processing was applied. Advantages of the thick film technology are: the possibility of large scale mass production (one can obtain several thousands sensor chips from one substratum) and the possibly automation of all steps of the sensor fabrication. The other distinctive advantage of the thick film technology is the stability characteristics of printed thick film layers. Several steps were undertaken in order to decrease the power consumption and optimize the construction of semiconductor gas sensors. (Kim J.H., 1997)

The used of two-side construction (see Figure 2) which allows miniaturization of the sensor chip. The final dimensions of the sensor chip were as small as 1.5 mm×0.3 mm×0.15 mm. The thickness of the alumina substratum was decreased up to 0.1 μm .

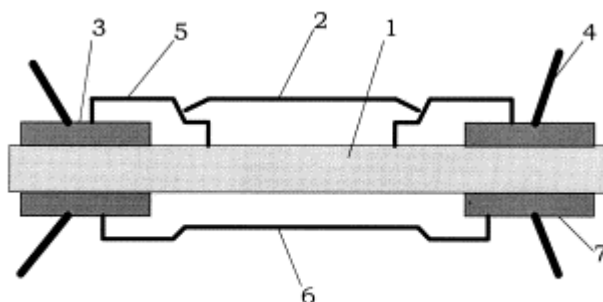


Figure 1: Structure of developed sensor. 1, Alumina substratum; 2, sensing layer; 3, contact pads; 4, connecting wires; 5, disjunction layer; 6, heater; 7, contact pads.

For the preparation of tin oxide powder, an oxalate method with an original preparation process was followed. After the precipitation the powder was dried at 500°C for 2 h. Then, an averaged particle size was observed as about 0.1 μm by SEM pictures as shown in Figure 3 (a) and the specific surface area was measured as approximately 18 $\text{m}^2 \text{g}^{-1}$ by BET method. (Kim J.H., 1997)